

FUEL ADDITIVE COMPOSITION AND ITS PREPARATIONTechnical field

5 The present invention relates to a fuel additive composition for the reduction/removal of vanadium-containing ash deposits, a process for the preparation of such a composition and the use of certain inorganic oxygen-containing metal compounds as a component of such a composition. More particularly the present invention relates to a fuel additive composition for the reduction/removal of vanadium-containing ash deposits in gas turbines and other by combustion of vanadium-containing fuel driven apparatuses, a process for its preparation and the use of certain inorganic oxygen-containing  
10 metal compounds as an active component thereof.  
15

Background art

Fuels such as unrefined crude oil and residual oil containing  
20 large amounts of impurities, which result in corrosive deposits in apparatuses driven by the combustion of such fuel. One such impurity is vanadium, which forms catastrophically, corrosive low-melting slag. Said slag can destroy vital parts within a short time. Crude oils usually contain vanadium in  
25 an amount within the range of 1-500 ppm depending on the source of the oil. Because of its origin as a concentrate from the refining process, residual oil contains several times more vanadium than the crude from which it is derived. Combustion of such vanadium-containing fuels primarily results in the formation of vanadium pentoxide,  $V_2O_5$ , which  
30 melts at about 675°C. In molten state  $V_2O_5$  behaves as an excellent solvent for e.g. the metal oxides that high temperature alloys used in the hot section of gas turbines form in order to protect their surfaces. Thus molten  $V_2O_5$ , acting as  
35 a solvent, strips away said metal oxides. The metal atoms on the surface of the gas turbine section in contact with the combustion gases respond by forming a new layer of oxide coating which is again stripped away by the  $V_2O_5$  and so on.

In gas turbines metal temperatures can be higher than 1000°C at which temperatures corrosion can proceed very fast so that the hot section may be destroyed within a week if no measures are taken to inhibit the corrosion cycle.

5

In order to overcome the corrosion problems caused by  $V_2O_5$  the so-called oil soluble magnesium products were developed. These products are based on the ability of magnesium compounds to react with  $V_2O_5$  to form a vanadate. Early products  
10 belonging to this group contained magnesium naphthenates which in the next step of development were replaced by compositions based on magnesium sulfonates. The third generation of oil soluble magnesium products comprises magnesium carboxylate products.

15

Thus, for instance, US RE 32653 discloses a method for the preparation of a magnesium-containing complex by heating, at a temperature above about 30°C a mixture consisting essentially of

20

(A) at least one of magnesium hydroxide, magnesium oxide, hydrated magnesium oxide or a magnesium alkoxide;

(B) at least one oleophilic organic reagent consisting essentially of an aliphatic cycloaliphatic or aromatic carboxylic acid containing at least eight carbon atoms or an

25

ester or alkali metal or alkaline earth metal salt thereof;

(C) water; and

(D) at least one organic solubilizing agent for component B.

30

The oil soluble magnesium products are added to the fuel in an amount sufficient to convert  $V_2O_5$  to magnesium orthovanadate,  $Mg_3V_2O_8$ , which melts at above 1100°C. Said temperature is below the typical gas turbine temperature when introducing the additive composition in the combustion chamber, but above  
35 the turbine gas inlet typical temperature due to the flame cooling process. Thus there will be no liquid  $V_2O_5$  that will act as a solvent for the alloy surface metal oxides and thus corrosion caused by  $V_2O_5$  is inhibited.

The first generation of oil soluble magnesium products had a concentration of magnesium as low as about 4%. The concentration was increased in the second generation up to about 14% magnesium and in the third generation the concentration could be raised further. However, there is a continued need for fuel additive compositions with still higher concentrations of magnesium or other metals capable of forming vanadates having a melting point above that of vanadium pentoxide.

Moreover, these prior art compositions give a dense vanadate deposit the removal of which may cause some trouble.

As an alternative to oil soluble magnesium products US-A-4 412 844, issued November 1, 1983, suggests oil dispersible aqueous dispersions of magnesium hydroxide comprising in percentages by weight:

(a) 20-70% magnesium hydroxide having particle size from 1.0-50 microns;

(b) 29-79% water;

(c) 1.0-8.0% of a water-dispersible, oil-soluble, water-in-oil emulsifying agent having an HLB value of from 4-10;

(d) 0.1-6% of a water-soluble, oil-dispersible emulsifying agent having an HLB of from 20-40.

Such slurries do not allow chemical high efficiency inhibition for ash melts due to the large crystal size. This patent states the preferred particle size to be in the range of about 30-2 microns, which makes the composition only practically applicable per se to boilers. Thus it is expressly stated that the magnesium hydroxide slurry specifically disclosed in the working example "would be utilized to control vanadium corrosion in a utility boiler".

In addition such slurries have a limited stability.

Accordingly, it is an object of the present invention to provide a fuel additive composition containing a high concentration of magnesium or other metal capable of forming vanadates  
5 having a melting point above that of vanadium pentoxide.

It is another object of the present invention to provide a fuel additive composition, which on use gives a porous vanadate deposit that is easily removed.  
10

It is a further object of the present invention to provide a fuel additive composition, which is stable for a long time such as 12 months and longer at ambient temperature.  
15

These and other objects are achieved by means of the fuel additive composition and the process for its preparation according to the present invention.

## 20 Summary of the invention

The present invention is based on the discovery that crystalline particles of inorganic oxygen-containing metal compounds which when suddenly being subjected to high temperatures almost "explosively" liberate a gaseous substance by evaporation, such as water vapour or carbon dioxide in case of e.g. magnesium hydroxide and magnesium carbonate, respectively, and are converted to particles of the corresponding metal oxide having a structure of increased porosity and reduced density when compared to a corresponding oxide prepared by  
25 evaporation of gas at considerably lower temperatures. This makes the oxide better suited for reaction with vanadium pentoxide will percolate easier into the more porous particles. The presence or formation of such more porous particles admits a faster chemical reaction due to the fact that the ions  
30 of  $V_2O_5$  can travel much faster from the surface of the porous particles along the pores surface of the lattice of said par-

ticles as vanadate forms than in the denser lattice of non or low porous crystalline oxide.

It was also surprisingly found that when using an inorganic oxygen-containing metal compound, which liberates a gaseous substance by evaporating when being suddenly subjected to the heat of a combustion flame, or a porous low density oxide with a particle size distribution essentially within the range of from 0.1 to 2 micron as the active ingredient of a fuel additive composition the vanadate deposit formed was much easier to remove than the vanadate deposit formed when using prior art compositions.

The said particle diameter less than 1-2  $\mu\text{m}$  as a measurement of particle size is just a rough indicative measurement, as total mass, density, shape and porosity are important "size" properties to be considered as optimizing a fuel additive dispersion and its functional properties on ash melts and corrosion inhibition as well as deposit problems concerned. The optimal "size" in all the size dimensions named will minimize deposit buildups due to the particles kinetic adsorption/desorption rate, preferably approaching 1,0 and thereby avoiding high adsorbing atomized and  $<\sim 100$  nm and avoiding high impaction rate into deposit by dense particles above the upper,  $>1000$  nm, micron sized limit.

Moreover, it was found that by proper selection of the dispersing system, for an oil soluble solvent system, avoiding water to the largest extent possible and using a specific process for the preparation of the fuel additive composition, it was possible to increase the level of the concentration per volume unit of the metal to a level not having been disclosed previously for submicron and nano-sized additives. Thus, according to the invention a combination of at least one liquid selected from the group consisting of liquids soluble in oil on one hand and at least one dispersant selected from the group consisting of low molecular weight dis-

persants and high molecular weight dispersants on the other is used as the dispersing system.

Thus, in accordance with a first aspect of the present invention there is provided a fuel additive composition for the reduction/removal of vanadium-containing ash deposits in gas turbines and other by combustion of vanadium-containing fuel driven apparatuses, which composition as its active ingredient comprises a compound of a metal capable of forming a vanadate with vanadium of said ash deposits, which composition comprises

a) as said compound of a metal capable of forming a vanadate with vanadium of said ash deposits a1) an inorganic oxygen-containing compound of said metal in particle form, which oxygen-containing compound, when heated up in a combustion flame, liberates a gaseous substance by evaporation and forms the corresponding metal oxide having a crystalline porous low density structure, or a2) said corresponding metal oxide having a crystalline porous low density structure, said inorganic oxygen-containing compound a1) and said corresponding metal oxide a2) having a particle size distribution essentially within the range of from 0.1 to 2 micron, preferably from 0.1 to 1 micron and said corresponding metal oxide a2) having a density of at most 2.0 g/cm<sup>3</sup>,

dispersed in

b) at least one liquid selected from the group consisting of liquids soluble in oil,

by means of

c) at least one dispersant selected from the group consisting of low molecular weight dispersants and high molecular weight dispersants.

According to another aspect of the present invention there is provided a process for the preparation of a fuel additive composition according to the invention, which process comprises

- 5 mixing a powder of an inorganic oxygen-containing compound of a metal capable of forming a vanadate with vanadium of ash deposits from vanadium-containing fuel and which inorganic oxygen-containing compound when heated up in a combustion  
10 flame liberates a gaseous substance by evaporation to form the corresponding oxide having a crystalline, porous low density structure or a powder of said oxide having a crystal-  
line porous low density structure into a mixture of at least one liquid selected from the group consisting of liquids  
15 soluble in oil with at least one dispersant for said inorganic oxygen-containing compound or oxide selected from the group consisting of low molecular weight dispersants and high molecular weight dispersants using shear forces to form a homogenous pumpable premix and  
20  
subjecting the premix to a treatment comprising size degradation and dispersant coating to a particle size distribution of the inorganic oxygen-containing metal compound and oxide essentially within the range of from 0.1 to 2 micron, preferably from 0.1 to 1 micron, under centrifugal or oscillation  
25 forces in the presence of a grinding medium and/or ultrasonic treatment until a plot of the sediment height in samples taken periodically during said treatment and centrifuged at a fixed rate for a fixed period versus time plateaus and the  
30 viscosity has decreased and come into a steady state.

- In accordance with a further aspect of the present invention there is provided the use of an inorganic oxygen-containing compound of a metal selected from the group consisting of  
35 metals capable of forming vanadates having a melting point within the range of from 650°C to 2000°C with vanadium of ash deposits from vanadium-containing fuel, which inorganic oxygen-containing compound when heated up in a combustion flame

liberates a gaseous substance by evaporation to form the corresponding oxide having a crystalline, porous low density structure, or the corresponding oxide obtained by heating the inorganic oxygen-containing compound at a temperature which  
5 is high enough to give the oxide in crystalline porous low density state but is below the melting point of the oxide, said inorganic oxygen-containing compound and said crystalline porous low density oxide having a particle size distribution essentially within the range of from 0.1 to 2 micron,  
10 preferably from 0.1 to 1 micron, as a component of fuel additive compositions for the reduction/removal of vanadium-containing ash deposits.

#### Detailed description of the invention

15

Vanadium-containing fuels are used within several fields of apparatuses driven by the combustion of fuel. The corrosion problems caused by the presence of vanadium may be most serious in the case of gas turbines but such problems also exist  
20 in connection with e.g. boilers and diesel engines, wherein the metal temperatures are lower than in gas turbines and relatively less hazardous but still serious corrosion problems compared to gas turbines exist.

25 According to the present invention the metal of the inorganic oxygen-containing compound or oxide to be used in the invention should be chosen so that on reaction with the vanadium pentoxide a vanadate is formed that has a melting point exceeding the temperature at which the composition is used.  
30 Thus, in case of gas turbines a metal should be chosen the melting point of the vanadate thereof preferably exceeds 1100°C. Examples of such metals are magnesium the vanadate of which melts above 1100°C and yttrium the vanadate of which has a melting point above 1800°C, magnesium being the preferred metal of these two metals for economical reasons. Ex-  
35 amples of other vanadates having melting points enabling their use in the compositions according to the invention to be used in connection with apparatuses of lower temperature



are among others, solely or in combinations, aluminum, zirconium, manganese, iron, copper, nickel and calcium. Often other metals than e.g. magnesium are either both rare and expensive or are environmental pollutants, e.g. manganese etc.

5

Depending on the specific field of use generally metals capable of forming vanadates having a melting point within the range of from 650°C to 2000°C.

- 10 Due to contaminants present in the fuel the vanadates formed may be contaminated therewith resulting in a decrease or an increase of the melting point in comparison with 100% pure vanadate. Consideration should be paid thereto when selecting the metal compound or oxide used in the composition according  
15 to the present invention.

In accordance with one embodiment of the fuel additive composition according to the present invention the active ingredient thereof comprising an inorganic oxygen-containing compound of a metal capable of forming a vanadate with vanadium  
20 of ash deposits is a hydroxide of said metal which hydroxide when heated up in a combustion flame is converted to the corresponding oxide having a crystalline porous low density structure.

25

As indicated previously, hydroxides such as, for instance, magnesium hydroxide, may be dehydrated almost "explosively" at very high temperatures (over 1000°C and below 2800°C) to form the corresponding metal oxide. Unlike the oxides formed  
30 by dehydration of hydroxides at lower temperatures (such as just above the dehydration point of 350°C for the conversion of magnesium hydroxide to magnesium oxide) resulting in oxides with a more dense crystalline structure the oxides formed at the higher temperatures [below the upper limit in  
35 the "dead burned" range where the oxide density closely approaches the maximum density] are more porous and have a less dense crystalline structure than else.

According to another embodiment of the fuel additive composition according to the present invention said inorganic oxygen-containing compound of a metal capable of forming a vanadate with vanadium of ash deposits is a metal carbonate.

5 When suddenly being heated at high temperatures such as in a combustion flame the carbonate will liberate carbon dioxide and form the corresponding metal oxide having a crystalline porous low density structure analogously to the formation of the oxide from an hydroxide at very high temperatures.

10

According to a further embodiment of the fuel additive composition according to the present invention said compound of a metal capable of forming a vanadate with vanadium of ash deposits is a metal oxide having a crystalline porous low density structure. Such oxides may, for instance, be prepared from the corresponding hydroxides or carbonates by heating at a high temperature. In order to obtain maximum porosity of the oxide the conversion of the hydroxide or carbonate should be carried out below the point at which the oxide tends to increase in density, but close thereto and far below it starts melting. Above said point at which the oxide "tends to start melting" the pore structure continually decreases as approaching the critical melting point, at which maximum density will be reached, for e.g. magnesium oxide at 2750°C.

15  
20  
25 Such a heat treatment to achieve minimum porous density oxide may be performed by passing a dry powder of an optimal size distribution of the hydroxide or carbonate through a flame having a temperature suitably adapted below the density decreasing point of the oxide as indicated above.

30

Alternatively, low density metal oxides may also be prepared by suddenly subjecting submicron sized crystals of an inorganic oxygen-containing metal compound, preferably a hydroxide or a carbonate, which when heated to a high temperature liberates a gaseous substance by evaporation, to heating at an appropriately high temperature in an oven. Thus, for instance, the present inventors rapidly heated sub-micron sized particles of magnesium hydroxide in an oven at a temperature

35

of 1000°C for a short time which resulted in the conversion of the magnesium hydroxide into magnesium oxide having a density of  $\sim 1.4 \text{ g/cm}^3$ . Similar heating of magnesium carbonate in an oven at a temperature of 1300°C resulted in magnesium  
5 oxide having a density as low as  $1.03 \text{ g/cm}^3$

According to the present invention the low density metal oxide should preferably have a density of at most  $2.0 \text{ g/cm}^3$ , more preferably below  $1.5 \text{ g/cm}^3$  and most preferably below  $1.0$   
10  $\text{g/cm}^3$ .

The inorganic oxygen-containing metal compounds and porous low density metal oxides incorporated in the fuel additive composition according to the invention should have a particle  
15 size distribution essentially within the range of from 0.1 to 2 micron, preferably from 0.1 to 1 micron, preferably narrowly distributed close to the optimal size within that range of 0.1 to 1 micron. Preferably said compounds and oxides  
20 should have a particle size optimal distribution which is adapted to be most effective at the temperature at which a solid, porous metal vanadate is formed and to form ash particles which deposit as little as possible [due to thermodynamic surface adsorption and desorption properties of the  
particles] and form as loose a deposit as possible [due to  
25 the porosity of the particles and thereby the epitactic and topotactic deposits lattice build-up structure].

According to the high initial flame maximum temperature in the range of 1600-2000°C before cooling the gas the particle  
30 size distribution should be selected so that the metal vanadates formed in the flame are not given sufficient time to melt before reaching areas of the apparatus having a temperature below the melting point of the vanadates. Moreover, the porous oxides added to the fuel are not delayed in their re-  
35 action to the formation of the vanadates in the heat zone compared to the porous oxides formed from, for instance hydroxides or carbonates bypassing the heat zone. This means that in case of gas turbines in which the temperature of the

flame may be as high as around 2000°C, a hydroxide or a carbonate should be used which has a particle size which is greater than that of the same hydroxide or carbonate to be used in apparatuses operating at a lower heat zone flame temperature. Furthermore, due to their higher reactivity surface enlarged porous metal oxides should be used at temperatures lower than those prevailing in gas turbine heat zones, i.e. they may preferably be used in boilers and diesel engines if an extraordinarily low operating temperature in the heat zone would be a disadvantage of the addition of the heat zone by passing metal hydroxide into the fuel.

Moreover, it was found that conversion of magnesium carbonate into magnesium oxide at a given temperature is a slower process than the conversion of magnesium hydroxide to the oxide due to the difference in energy required to evaporate the carbon dioxide from the carbonate in comparison with water from the hydroxide. This means that in apparatuses working at relatively low temperatures (e.g. boiler and diesel engines) the use of magnesium hydroxide particles may be the preferred choice whereas magnesium carbonate might be preferred for use in connection with gas turbines having an extremely high temperature in the flame in order to obtain a low density of the oxide formed.

Of specific importance is that the size of the oxide particles is in the range not below 0.1 micron and not above high density impacting 2 micron, preferably exhibiting a particle size distribution injected into the fuel around 0.4 to 0.5 micron, in order to reduce the deposit accumulation due to the Brown Movement Kinetic affecting the particles surface adsorption and desorption rate on the deposit surface and that the said particles have a surface area including internal pores surface interface area comparable to that of crystalline high density oxide particles of a particle size far below 0.1  $\mu\text{m}$  to maximize the reactive surface. Such a high surface area will solely be achievable by porous particles.

The inventors have noted that dehydration or evaporation of magnesium hydroxide particles at high temperature causes a split size reduction and volume expansion and agglomeration into a less tight particle size distribution depending on the particles individual initial size. For this reason the particle size of the particles used in the fuel additive compositions according to the invention will generally be distributed in a somewhat enlarged size range below and above when using the hydroxide in comparison with the use of a size tailored oxide.

The particles of the inorganic oxygen-containing compound as well as the oxide particles should preferably have a narrow (low variance) particle size distribution, preferably around a cross section largest distance arithmetic mean in the 0.2 to 0.5 micron range and with a variance for a lognormal distribution in the range  $\sim 0.2 < \delta < \sim 0.6$ .

In the fuel additive composition according to the present invention the inorganic oxygen-containing metal compound or oxide particles are dispersed in at least one liquid selected from the group consisting of liquids soluble in oil.

Contemplated for use in the fuel additive composition according to the invention are liquids selected from the group consisting of mineral oils, synthetic oils, highly aromatic naphtha, diesel oil, vegetable oils, esterified vegetable oils, animal oils and esterified animal oils.

Examples of vegetable oils and esters thereof to be used in the fuel additive compositions according to the invention include, but are not limited to, peanut oil, coconut oil, corn oil, linseed oil, rape-oil, palm oil, sunflower oil, olive oil, tall oil and esters thereof, the preferred representative thereof being rape-oil methyl ester (RME).

Examples of animal oils to be used in the fuel additive compositions according to the invention include, but are not

limited to, fish liver oil, train-oil and liquid modified fat from slaughter-houses.

5 The preferred representatives of the liquids soluble in oil to be used in the present invention are diesel oil and rape-oil methyl ester.

10 According to the present invention the inorganic oxygen-containing metal compound particles or metal oxide particles have become dispersed in at least one liquid which, as stated above, is selected from the group consisting of liquids soluble in oil by means of at least one dispersant selected from the group consisting of low molecular weight dispersants and high molecular weight dispersants.

15 The term "low molecular weight dispersants" as used here and in the claims is used to designate dispersants having a molecular weight usually within the range of from 1.000 to 2.000g/mole. In addition, dispersants may be classified to  
20 manifold properties as described below.

The term "high molecular weight dispersants" as used here and in the claims is used to designate dispersants having a molecular weight usually within the range of from 5,000 to  
25 30.000 g/mole.

In addition. the conventional low molecular weight dispersants are categorized according to their structure as anionic, cationic, amphoteric and nonionic. Their efficiency is defined by a) absorption of polar groups to the surface of the  
30 particles to be dispersed and b) the behavior of a non-polar chain of the medium surrounding the particle.

The dispersant industry supplies a huge variety of efficient  
35 steric dispersants that enables stable solid particle dispersions for colloid oil and aqueous systems. A colloid is a liquid droplet or a solid particle in the size range of at most 1-2  $\mu\text{m}$  but normally submicron or in the range of one

molecule to many molecules forming a size of 2 -999 nm in average diameter. Steric dispersants adsorb and coat the particle surfaces. A surface is an interface between two non-soluble compounds, one liquid and one solid state or two liquid states. As no interface or surface occurs between the dispersant-particles-layer-tails penetrating into the particles ambient solvent the colloid dispersion is a true dispersion formed of particles and such dispersions is commonly defined as a micelle dispersion. A huge group of steric dispersants forms micelles both in oil and water systems.

Most steric dispersants form micelles in a selected oil soluble solvent, when the hydrophobic tail penetrates into the solvent. The stability of such dispersions is depending on many different forces defining the stability boundaries for the other unit tail. The other said molecular hydrophilic tail adsorbs to the particle surface and will be bondable to the surface of the particle in many different ways due to the kind of (1) anchor groups, (2) the number of repeating units in the polymer and (3) if the dispersant is a homo polymers dispersants whereas the repeating units are of one kind or is a co-polymer of two different kinds and (4) the electrostatic properties.

The known art of the described colloid dispersion systems admits a suitable tool to tailor a stable composition of solid particles suitable as a fuel additive. In the range of suitable compounds magnesium carboxylates and magnesium sulfonates has been widely used to create stable metal oxide dispersions in fuel additives. In the disclosed invention the kind of dispersants suitable is enlarged to admit higher concentrations of stable solid dispersions. Among others we have tested Hypermer® LP4 (amine derivate of a fatty acid condensation polymer, from UNIQEMA, Everberg, Belgium) EFKA 4010 (modified polyurethane, from EFKA Inc., Heerenveen, the Netherlands) and Rhodafac® RE 610 (nonylphenol ethoxylate based phosphate esters, from Rhodia Inc, France). All of these dispersants among others fulfill the claim to form sta-

ble dispersions of magnesium oxides and magnesium hydroxides and other particles if a suitable solvent and dispersion technology is applied.

- 5 The selection of a dispersant for a specific application has to be done due to the different claims of stability due to ambient boundaries i.e., solid concentrations, temperature, g-forces and the desired viscosity for the composition. To achieve maximum particle concentration the dispersant layer  
10 that coats the particles has to be thin. This is achieved by a small low molecular weight dispersant as characterized by Rhodafac® RE 610 having two tail units penetrating into the solvent or Hypermer® LP4. When the volume of solvent in the composition increases and the particle concentration is lower  
15 it is suitable instead to choose a high molecular weight dispersant for instance EFKA 4010. When low particle concentrations are desired other dispersants may be preferably applied, but for such applications the particle size range is of basic importance due to solvent molecules Brown Movement  
20 Kinetics. In addition simple non-steric solely and electrostatic dispersants, such as low molecular waxy compound e.g. modified or non modified lanoline extracts from sheep wool fat-layer may be applied.
- 25 High molecular weight dispersants have pendent anchoring groups, which adsorb to the surface of the particles to be dispersed. Their mechanism of action is by hydrogen bonding, dipole-dipole interactions or Van der Waal forces. The polymeric framework is sufficiently great to give an effect  
30 called sterical stabilization.

The preferred dispersants to be used in the present invention are anionic and amphoteric low molecular weight dispersants.

- 35 Although, anionic low molecular weight dispersants to be used in the present invention include magnesium soaps of carboxylic and sulfonic acids. Such dispersants and comparable dispersants containing magnesium are not preferable, as they may



comprise atom sizes magnesium that depart from the scope of porous oxides feature, as a partial or total disadvantage to the aimed invention.

- 5 The fuel additive composition according to the present invention will generally comprise the submicron or nano-sized inorganic oxygen-containing metal compound or oxide (component a)) in a concentration of from 10 to 65% by volume, preferably from 20 to 50% by volume and more preferably from 30 to  
10 50% by volume, and most preferably from 40 to 50% by volume, calculated on the total volume of the compositions, the balance to 100% by volume essentially consisting of components b) and c) and possibly a minor amount of water (generally less than 0.5% by volume) such as moisture emanating e.g.  
15 from the use of not fully dry starting materials, such as the hygroscopic substance magnesium hydroxide or deliberately added to regulate the viscosity and stability of the composition.
- 20 The upper limit of the concentration of inorganic oxygen-containing compound or oxide in each specific case is defined by the particle volume size and specific dispersants depletion limit due to the specific particle size that may destabilize the dispersion. Thus the upper limit will increase  
25 with increasing average particle size. Thus, for instance, the upper limit will be around 50% by volume in case of particles having a particle size low variance distribution, as a distribution having variance from ~0.2 to ~0.6 for the log-normal distribution around a mean size from 500 to 200 nanometers (nm) respectively  
30

The volume ratio component b) to component c) generally depends on the specific substances used as those components and the amount of particles to be dispersed. The optimum ratio in  
35 each specific system may easily be determined in a series of experiments varying said ratio for which experiments no inventive activity should be required.

The fuel additive composition according to the invention is prepared according to said another aspect of the invention by means of the process according to the invention, which process comprises

5

mixing a powder of an inorganic oxygen-containing compound of a metal capable of forming a vanadate with vanadium of ash deposits from vanadium-containing fuel and which inorganic oxygen-containing compound when heated up in a combustion  
10 flame liberates a gaseous substance by evaporation to form the corresponding oxide having a crystalline, porous low density structure or a powder of said oxide having a crystalline porous low density structure into a mixture of at least one liquid selected from the group consisting of liquids  
15 soluble in oil with at least one dispersant for said inorganic oxygen-containing compound or oxide selected from the group consisting of low molecular weight dispersants and high molecular weight dispersants using shear forces to form a homogeneous pumpable premix and

20

subjecting the premix to a treatment comprising size degradation and dispersant coating to a particle size distribution of the inorganic oxygen-containing metal compound and oxide essentially within the range of from 0.1 to 2 micron, preferably from 0.1 to 1 micron, under centrifugal or oscillation  
25 forces in the presence of a grinding medium and/or ultrasonic treatment until a plot of the sediment height in samples taken periodically during said treatment and centrifuged at a fixed rate for a fixed period versus time plateaus and the  
30 viscosity has decreased and come into a steady state.

35

Metal compound particles to be used in the process according to the present invention should not contain crystal water and have a low moisture content, if necessary obtained by a drying process, preferably a moisture content far below 0.5% by weight.

The particle size of the metal compound or oxide particles should not be exceedingly greater than the size of the particles of composition prepared by means of the process and generally particle sizes within the submicron range should be used, but small particles of a substantial amount below 0,1 microns easily adsorbing the deposit areas and having a low desorbitions rate should be avoided.

According to a preferred embodiment of the process according to the present invention the particles of the metal compound or oxide are added to a vessel containing a mixture of said at least one liquid selected from the group consisting of liquids soluble in oil and at least part of said at least one dispersant under mixing to form a premix allowing the temperature to rise during the mixing, e.g. to a temperature within the range of from 50°C to the upper limit ~85°C defined by the centrifugal forces and the viscosity to avoid cavitation of the grinding media in order to reduce the viscosity of the premix.

For the procedure of the second step of the process according to the present invention preferably a basket mill is used. Such mills are available on the market and are, for instance, sold in different models under the trade name Turbomill by Mirodur SpA, Aprilia, Italy.

The grinding media used are e.g. small zirconium balls, the diameter of which is chosen in accordance with the intended particle size of the metal compound and oxide particles, respectively, after grinding so that said diameter is increased when larger particles are wanted. Generally said diameter will be within the range of from 0.8 to 1.2 mm, however, balls of uniform size being used in each specific case. Balls of other materials known as suited for use as grinding media, e.g. steel and glass, can also be used in the process according to the invention.

A zirconium ball size of 0.8 mm is, for instance, sufficient to reach the desired size for e.g.  $\text{Mg}(\text{OH})_2$ -particles and efficiently disperse the particles in accordance with the invention.

5

The premix mentioned above is filled into the basket mill vessel and rotating is started and speeded up to full power loading allowing temperature to rise to about 75-85°C. All moisture that evaporates during the basket mill operation  
10 should be evacuated from the vessel.

Samples are taken at intervals of 30 to 70 minutes such as 1 hour and centrifuged at a fixed rate, e.g. within the range of from 2000 rpm to 4000 rpm, such as 3000 rpm, for a fixed  
15 period within a range of from e.g. 30 minutes to 1 hour, such as 45 or 50 minutes, and the height of the sediment of each sample measured. During rotation of the basket the height of the sediment of the different centrifuged samples will start to decrease rapidly as sampling proceeds. Rotation is contin-  
20 ued during a constant temperature operation phase until the plot of sediment height versus time plateaus and thereby the basic viscosity has decreased and come into a steady state.

As an alternative to the rotating basket mill operation  
25 grinding may be performed by means of oscillation buckets. Alternatively or as a supplement to grinding ultrasonic treatment may be applied.

The design of grinding mills commonly supplied has to be ad-  
30 justed for the engine effect upwards to achieve at least an accelerative force above 50 g on the liquid to reach the limit force needed to override the tensions to disaggregate the present smallest nano particles. Preferably 70 g is needed as desired to economically optimize the capacity dis-  
35 persed per kWh etc.

The liquid lubricant film must hold the balls of e.g. a basket mill apart from each other. Otherwise the cavitating

balls will degrade themselves rapidly. There is no possibility to achieve static pressure to degrade agglomerates and grind nano-scaled particles. The force here transmitted, to achieve degradation has to be transmitted to the electromagnetic interference between particle surfaces and the intermediate liquid.

A media mill optimizing the following parameters preferably achieves this.

10

1. Temperature
2. Relative content of solids in the liquid
3. Ball size
4. Ball density
- 15 5. Ball volume relative to inlet power to be transmitted.
6. Accelerative force in g-number (Af)

Media disc mills are not suitable as accelerative force achievable is too low.

20

Commonly in the color industry applied basket mills e.g. a Turbomill is suitable for the present purpose. But other kinds of mills as e.g. high frequency oscillation ball media vessels as e.g. the Colorox mill may be applied. By rotating the ball filled basket in a Turbomill the acceleration force (a) will be distinctly controlled by the rotation speed.

25

Equation (1)  $a = (\omega^2 * r * 2 * \pi)$ ; m/s<sup>2</sup>

Where:  $r$  = peripheral radius in meter for the basket  
or a body orbit

30

$\omega$  = angular velocity = rpm/60 = cycles per second = Hertz

and 1 Newton = 1 m/s<sup>2</sup>; and Af = a/9.82; g

35 As recognized by equation (1) the acceleration force is proportional to the radius for a body motion in a circular orbit and proportional to the square power for the angular velocity. Thereby, the needed rpm or frequency for different or-

bits to reach the acceleration to override the tension is given by:

Equation (2)  $\omega = \text{Square root of } (Af \cdot 9.82 / r) \text{ divided by}$   
5  $(2 \cdot \pi \cdot 60)$

An acceleration force (Af) of 70g is preferable to exceed the tensions in the crystal aggregate. Thereby equation (2) tells us the orbit frequency for different kind of mills and other  
10 kinds of power transmission facilities. As we decrease the orbit radius to a certain limit e.g. 10 mm we cannot apply the power by centripetal force as in a basket mill of understandable reasons. Instead an high frequency oscillatory or vibrato vessel is preferable. A 210 mm radius basket needs a  
15 rotating speed of 546 rpm to achieve a peripheral force of 70g. A small body in 10 mm radius oscillatory vessel needs a rotation speed of 3541 rpm or 59 Hertz.

To roughly define the velocity property limit to be override  
20 for different kinds of force transmission equipment in accordance with the invented process to prepare the dispersion for the invented composition we need the illustrative tube. Imagine a tube that enables to apply accelerative force in inversed direction for the liquid in one direction and the tube  
25 wall in the other direction. Thereby the relative speed and the tension between the liquid and the tube wall will define the sheer forces interfering the particles. As the entire volume in an oscillatory vessel will oscillate in small orbits the relative speed will reach approximately a maximum of  
30 twice the peripheral oscillation speed. Thereby the shear force limit will be reach at a frequency of 2504 rpm or 42 Hertz for a 10 mm radius oscillatory vessel instead of said frequency of 59 Hertz above for a single small body acceleration of 70g.

35

In addition ultrasonic methods may be used, as dispersion par se is desired. Similar to the oscillatory vessel case equation (2) will help us to define the frequency for different

ultrasonic amplitudes or wavelengths to be applied. As a conventional ultrasonic frequency is 20-40 kHz for e.g. 35 kHz the desired amplitude is 15 nm, but a substantially higher amplitude in the range above 1-10 microns is a necessity due to achieve sheer beams for the entire particles and not only for a small limit part on a particles surface area. The amplitude has to substantially exceed the particles size to admit surface coating and particles to cavitate. Thereby, ultrasonic equipment is also contemplated for use in the present invention, especially as increased power density is needed to achieve efficient fast coating on the small part of the very small nano particles to get a fully stable dispersion not reaggregating.

The invention will now become illustrated by means of a number of non-limiting working examples illustrating the preparation and use of the compositions according to the invention.

20

### **Examples**

#### **Materials used in Examples 1 & 2**

The magnesium hydroxide used was Ankermag®-HH from Magnifin Magnesiaprodukte GmbH, Austria. The magnesium powder contains > 98.0 % by weight (wt%)  $\text{Mg}(\text{OH})_2$  and < 0.5 wt% water. Specific surface 9-12  $\text{m}^2/\text{g}$  equivalence a mean size for a dense sphere diameter range from 200-260nm or in fact the largest diameter of the thin flakes crystals average ~500nm. The crystals D50 diameter is ~900 nm, i.e. the median size diameters in the distribution. In addition the crystal agglomerate upper limit diameter is less than approximately 50 microns. The preparation process according to the invention admits feeding by much larger particles, preferably a surface area above > 3-4  $\text{m}^2/\text{g}$ .

The dispersant used was Rhodafac® RE 610, from Rhodia Inc, France, which is characterized by the manufacturer as nonyl-phenol ethoxylate based phosphate esters.

5 Rape-oil methyl ester was supplied by Svenska Ekobränslen AB, Sweden.

**Example 1: Preparation of fuel additive composition-batch of 1000 kg**

10

20 kg of Rhodafac® RE610 and 270 kg of rape-oil methyl ester (RME) having a moisture content of <0.05% by weight were mixed in a dissolver vessel (Disolver DTM49 from Westerlins Maskinfabrik AB, Malmö, Sweden) to a homogenous mixture.

15

Then 690 kg of magnesium hydroxide powder dried to a moisture content of <0.5% by weight were gradually added under continued mixing allowing the temperature to rise to about 50°C to form a premix.

20

The premix was then transferred to the vessel of a basket mill (Turbomill® 2, from Mirodur SpA, Aprilia, Italy, with an engine effect of 55kW) containing balls of zirconium having a diameter of 0.8 mm as the grinding medium and rotation of the  
25 basket was started and speeded up to full power loading.

The temperature was allowed to increase to 75°C-85°C, i.e. securely below the upper limit where the reduced viscosity achieved by the increase in temperature will allow the balls  
30 of the milling medium to touch each other by chance.

The temperature was kept stable until the samples taken at intervals of 1 hour and centrifuged at a rate of 3000 rpm for 50 minutes indicated a rapid decrease in the height of the  
35 pellet obtained by such centrifugation after approximately 4-6 hours, due to operation temperature and the applied centrifugal force. The basket mill was kept running until the



premix was fully dispersed which occurred as decreasing the rotation in accordance to the decrease in the height of the pellet obtained by centrifuging samples as above until approaching a steady state. Then additional 20 kg of Rhodafac®  
5 RE610 and 20 kg of rape-oil methyl ester (in addition, if desired 1-5 liter water may be added per ton to achieve increased stabilization of the particles) were added and the grinding process continued for approximately 15 minutes.

10 The completed process was shut down and the composition liquid was pumped into barrels and samples were collected. If desired for the specific applications the liquid composition is diluted by RME before barreling it up.

15 The Mg content by ash test was ~29% by weight and the  $Mg(OH)_2$  content was 69% by weight (~46% by volume) and the upper tail of the size distribution was below 1,0 micron and the main particle flakes shown by a standard scanning electronmicroscope were in the range 0.2-0.5 micron.

20

**Example 2. Preparation of fuel additive composition-batch of 1000 kg**

40 kg of a Rhodafac® RE610 and 270 kg of diesel (class 1)  
25 were mixed in a dissolver vessel (Disolver DTM49 from Westerslins Maskinfabrik AB, Malmö, Sweden) to a homogenous mixture

Then 690 kg of magnesium hydroxide powder dried to a moisture content of <0.5 % by weight were gradually added under continued mixing allowing the temperature to rise to about 50°C  
30 to form a premix

The premix was then transferred to the vessel of a basket mill (Turbomill® 2, from Mirodur SpA, Aprilia, Italy, with an  
35 engine effect of 55kW) containing balls of zirconium having a diameter of 0.8 mm as the grinding medium and rotation of the basket was started and speeded up to full power loading.

The temperature was allowed to increase to 75°C-85°C, i.e. securely below the upper limit where the reduced viscosity achieved by the increase in temperature will allow the balls of the milling medium to touch each other by chance.

5

The temperature was kept stable until the samples taken at intervals of 1 hour and centrifuged at a rate of 3000 rpm for 50 minutes indicated a rapid decrease in the height of the pellet obtained by such centrifugation after approximately 4-  
10 6 hours, due to operation temperature and the applied g-force. The basket mill was kept running until the premix was fully dispersed which occurred as decreasing the rotation in accordance to the decrease in the height of the pellet obtained by centrifuging samples as above until approaching a  
15 steady state. Then additional 40 kg of Rhodafac® RE610 (in addition, if desired 1-5 liter water may be added per ton to achieve increased stabilization of the particles) were added and the grinding process continued for approximately 15 minutes.

20

The completed process was shut down and the composition liquid was pumped into barrels and samples were collected. If desired for the specific applications the liquid composition is diluted by diesel oil before barreling it up.

25

The Mg content by ash test was ~29% by weight and the  $Mg(OH)_2$  content was 69% by weight (~46% by volume) and the size distribution of the upper tail was below 1,0 micron and the main particle flakes shown by a standard scanning electronmicro-  
30 scope were in the range 0.2-0.5 micron.

### Example 3. Comparison of structures of magnesium oxide

In order to compare the structure of magnesium oxide having  
35 an porous structure formed by subjecting magnesium hydroxide to a high temperature with that of magnesium oxide prepared by dehydrating magnesium hydroxide at a comparatively lower temperature the following experiment was carried out.

Three samples of magnesium hydroxide powder having a particle size distribution of mean 400 nm, an  $\delta=0.4$  for the lognormal estimated cross-section function and a moisture content of <0.5 % by weight and equal in weight were used. The samples  
5 were rapidly heated in an oven at a temperature of 450°C 1000°C and 1300°C, respectively.

Analyses of the 1000°C treated sample showed that the surface area increased from BET 8.66 m<sup>2</sup>/g for the hydroxide particles  
10 to BET, 10.38 m<sup>2</sup>/g for the porous oxide particles. The density decreased from approximately 2.3 g/cm<sup>3</sup> for the Mg(OH)<sub>2</sub> to 1.36 g/cm<sup>3</sup> (measured by a pycnometer) for the converted MgO crystals. This is below 40% of the density of nonporous MgO of 3.58 g/cm<sup>3</sup> and a remarkably low density.

15

The specific surface area for Mg(OH)<sub>2</sub> and MgO was measured by Multipoint Surface Area N<sup>2</sup>-gas at 77° Kelvin adsorption isotherm and pore distribution. The pore diameter at surface had its distinct high frequency with as micropores within the  
20 range 3.5-6.5 nm for the almost fully dense Mg(OH)<sub>2</sub> and for the converted low density MgO as mesopores within the range of 10-60 nm with the mode-frequency just below 30 nm

It was confirmed by X-ray diffraction (Cu, K;  $\alpha=1.54\text{\AA}$ ) that  
25 MgO has a solely crystalline lattice structure whereby the crystals are not to any degree an amorphous unordered structured crystal. Thereby the expanded and to some extent sintered crystals contain open pores through the crystal surface as well as closed pores within the crystals due to the low  
30 density and the small 20% increase in specific surface area as loosen 3/5 atoms out of the crystal volume.

The other two samples treated at 450°C and 1300°C confirm that the MgO density is temperature sensitive as density decreases by temperature within the temperature range below the  
35 high temperature dead burned range above approximately 1600°C. Thereby there may be a need to tailor size low density MgO particles for certain applications as the operating com-

bustion temperature will be below the optimal temperature to form desired low density MgO particles to reduce deposit buildups

- 5 Similary, magnesium carbonate was rapidly heated in an oven at a temperature of 1300°C and the density of the magnesium oxide thus formed was measured by a pyknometer and found to be 1,03 g/cm<sup>3</sup>
- 10 The results of the density measurements together with density values found in literature are summarized in the following table.

15 **Table**

Density of magnesium oxide formed by heating magnesium hydroxide and magnesium carbonate at different temperatures at ambient atmospheric pressure.

20

Temp. [°C]	Density of MgO from Mg (OH) <sub>2</sub> [g/cm <sup>3</sup> ]	Density of MgO from MgCO <sub>3</sub> [g/cm <sup>2</sup> ]	Remark
450	2.13	-	
1000	1.36	-	
1300	2.45	1.03	
2750	3.58	3.58	from literature

**Example 4**

- 25 A fuel additive composition according to the present invention was used in a large-scale comparative test in a power plant, wherein two comparable 120 MW gas turbines were applied in parallel, both being fed with the same fuel until

injecting the composition according to the invention and a prior art composition (KL 200 from Baker Petrolite, USA), one for each gas turbine with the same present common pumps into the oil flow on its final short way into the combustion chamber. The gas turbines were completely up kept at onset including new turbine blades.

The fuel additive composition according to the invention used in this experiment had a density of  $\sim 1.56 \text{ g/cm}^3$  and contained  $\sim 69\%$  by weight of magnesium hydroxide particles and thereby  $29\%$  Mg by weight having a particles size distribution around mean  $\sim 300\text{-}500 \text{ nm}$  with a variance mean for the lognormal distribution of  $\sim 0.4$  and  $4\%$  by weight of Rhodafac® RE610 from Rhodia Inc, France and  $27\%$  by weight of REM.

KL 200 is a magnesium oxide over-based magnesium carboxylate vanadium inhibitor with a density of  $1.22 \text{ g/cm}^3$  containing  $20\%$  Mg as specified by the supplier.

Based on laboratory test figures every second hour the dose rate was maintained at the level of 2 grams of magnesium per 1 gram of vanadium inherent in the washed heavy fuel oil containing 20-30 ppm vanadium and  $\sim 2\%$  sulfur.

Inspections were made after each wash cycle.

The wash cycle is the time range from start of operation until the gas turbine needs to be cleaned up for deposits due to technical and economical disadvantages from the accumulated deposits of ash compounds.

It was found at the inspections for the 1<sup>st</sup> wash cycle before auto wash that the deposits were easy to remove by hand in case of using the composition according to the invention but could not be removed by hand in case of using the prior art composition.

During the 1<sup>st</sup> wash cycle in this comparative large-scale test, the input-output efficiency rate adjusted by uncontrolled variables shows an increase in average MWh output per unit oil of approximately 1% in favor to the turbine injected with the additive in accordance with the invention. Thereby, it was assumed that the gas turbines run in parallel with the same fuel was comparable. The 1% efficiency difference between the gas turbines was an underestimation of the true benefits of the invented composition as illustrated in the next paragraph.

During the 4<sup>th</sup> and 5<sup>th</sup> wash cycles both turbines were run with the prior art fuel additive to indicate the comparability. A difference was found. Instead of the comparison after the 1<sup>st</sup> wash cycle the 3<sup>rd</sup> and 6<sup>th</sup> wash cycles for the gas turbine run by the fuel additive according to the invention were compared to the 4<sup>th</sup> wash cycle run by the prior art fuel additive. It was found that the average efficiency increased in an amount of at least 2-4% by using the fuel additive composition according to the present invention.

Of special interest is the effect occurred as the turbine was tripped on the day 8 and the booster effect increased the efficiency by more the 2% units.

The volume of the pores in the deposits was estimated before auto wash. By letting a liquid be absorbed into deposit pieces it was found that deposits in accordance with the invention were substantially more porous in the range of an additional pore volume for deposit comparable locations of 30-115% and in accordance with that a decreased density in the range up to 25% was reported. In addition the liquid absorbance speed was much faster for the deposits in accordance with the invention.

Of great importance is the ability of the deposits to absorb aerosol water during auto wash and booster tripping a gas turbine. Indicatively this feature is in proper advance for

deposits formed by applying the invented composition as the absorbance of H<sub>2</sub>O from ambient 60% relative humidity air rapidly reaches a steady state of 2.9% compared to the absorbance of deposits formed by the prior art conventional composition which was more than 10 time less or 0.25% H<sub>2</sub>O at room temperature.

### Conclusions

10 The findings illustrated in the examples show and fully explain the better off for gas turbine input-output efficiency for the porous MgO-particles applied in accordance with the present innovation to react in the combustion chamber instead of MgO dense-structured crystals as mainly is inherent in the  
15 combustion chamber for prior art compositions. These findings may be generalized to other solid metal-oxides, from the scientific common sense in chemistry and physics. Thereby, additional metals not tested may be applied in accordance with the disclosed invention to reduce the negative efficiency impacts of hard ash deposits in oil power transformation.  
20

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many modifications, alterations  
25 and substitutions are possible in the practices of this invention without departing from the spirit or scope thereof as defined in the appended claims.